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(54) Clay filler for elastomers

(57) A filler for use in elastomer compositions comprises a substantially dehydroxylated clay, having a specific gravity not greater than 2.4 and a specific surface area of at least $10 \text{ m}^2\text{g}^{-1}$. The substantially dehydroxylated clay, which is preferably treated with a substituted silane, can be obtained by calcining a kaolinitic clay at a temperature below 1100°C for up to about 5 seconds. The elastomer can be natural or synthetic rubber.

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SPECIFICATION

Improvements in or relating to fillers and their use in elastomer compositions

- 5 This invention relates to fillers for elastomers, such as natural and synthetic rubbers, and to elastomer compositions containing them. 5

Most mineral fillers which are commonly available provide only a relatively small improvement in the strength of an elastomer composition in which they are incorporated because of their relatively coarse particle size or because of the weak chemical affinity between the elastomer and the surface of the filler particles, or a combination of these two factors. Currently the most widely used reinforcing filler for elastomers is carbon black which is a very finely-divided material and, on account of the hydrophobic nature of its surface, has a good affinity with elastomers, the presence of the carbon black in an elastomer composition giving a good increase in the strength of the elastomer. 10

15 A particularly stringent duty for elastomer compositions is in the manufacture of motor vehicle tyres. Carbon black is almost exclusively used as the filler in these compositions because of its very good reinforcing properties. A rubber compound used for motor vehicle tyres must have good tensile strength properties, good tear strength and good resistance to abrasion. It must also not be subject to significant permanent deformation after tension or compression. Such permanent deformation is generally known in the art as "permanent set". Permanent set may be measured after subjecting a sample of the compound to tension, in which case it is known as "tension set", or after compression, in which case it is known as "compression set". However carbon black is most commonly prepared by burning oil under controlled conditions and is therefore likely to become increasingly expensive and in short supply. Attempts have been made to find a satisfactory replacement for carbon black and for this purpose it has been proposed to use *inter alia* kaolin clays, usually after treatment with an organosilane, see for example British Patent Specification Nos. 882,058; 948,163; 1,062,595; 1,272,287 and 1,430,125 and United States Patent Specification No. 3,290,165. Whilst these known organosilane-treated kaolin clays have enhanced reinforcing properties as compared with the untreated materials, 25

30 they do not constitute a satisfactory replacement for carbon black in many applications. According to the first aspect of the present invention there is provided a filler, for use in elastomer compositions, which filler comprises a substantially dehydroxylated clay which has a specific gravity not greater than 2.4 and a specific surface area (as measured by the B.E.T. liquid nitrogen absorption method) of a least $10 \text{ m}^2\text{g}^{-1}$.

35 The B.E.T. liquid nitrogen absorption method of measuring specific surface area is described in British Standard Specification No. 4359: Part 1: 1969. According to the second aspect of the present invention there is provided an elastomer composition which comprises an elastomer and a filler in accordance with the first aspect of the invention.

40 Preferably, the substantially dehydroxylated clay is a calcined kaolinitic clay having a specific gravity not greater than 2.2 and a specific surface area of at least $20 \text{ m}^2\text{g}^{-1}$. Advantageously, the dehydroxylated clay has a particle size distribution such that it contains at least 80% by weight of particles smaller than 2 microns equivalent spherical diameter.

45 The substantially dehydroxylated clay is advantageously treated with a substituted silane. Substituted silanes which have been found to be useful in the present invention include those containing at least one aminoalkyl or mercaptoalkyl group and at least one hydroxy, hydroxyalkyl or alkoxy group. Most preferably, the substituted silane is one which can be represented by the general formula:



60 wherein R_1 is an aminoalkyl or mercaptoalkyl group, R_2 is a hydroxy, hydroxyalkyl or alkoxy group, and each of R_3 and R_4 , which may be the same or different, is a hydrogen atom or a hydroxy, alkyl, hydroxyalkyl or alkoxy group. Most preferably, each of R_2 , R_3 and R_4 is a hydroxy, hydroxyalkyl or alkoxy group and each of R_1 , R_2 , R_3 and R_4 contains not more than 4 carbon atoms.

65 Generally, a calcined kaolinitic clay filler in accordance with the invention will be coated with 65

at least 0.05% by weight, and preferably at least 0.25% by weight, of the substituted silane. Usually, the amount of substituted silane used to coat the calcined kaolinitic clay is in the range of from 0.4% to 0.8% by weight based on the weight of dry calcined kaolinitic clay. The use of less than 0.05% by weight of the substituted silane gives an insignificant increase in the reinforcing properties of the calcined clay filler as compared with the uncoated calcined clay filler. On the other hand there is no advantage in using more than about 0.8% by weight of the substituted silane, and if more than about 2.0% by weight of the substituted silane is used, this causes cross-linking of the elastomer giving a brittle product.

One method of preparing a calcined clay filler in accordance with the first aspect of the invention comprises calcining a clay containing at least 60% by weight of particles smaller than 2 microns equivalent spherical diameter (e.s.d) by exposing the clay to a temperature in the range of from 500°C to 1100°C for a time not exceeding 5 seconds. Preferably, the clay contains at least 80% by weight of particles smaller than 2 microns equivalent spherical diameter. Thus, a filler in accordance with the first aspect of the invention can be prepared by fractionating or comminuting a pulverised kaolinitic clay so that it has a particle size distribution such that at least 80% by weight thereof consists of particles having an equivalent spherical diameter smaller than 2 microns, and thereafter calcining the kaolinitic clay by exposing it to a temperature in the range of from 500°C to 1100°C for a time not exceeding 5 seconds. Most preferably, the dry, pulverised kaolinitic clay is calcined by exposure to a temperature in the range of from 600°C to 900°C for a time of about 1 second. This procedure is conveniently carried out by injecting the kaolinitic clay into a combustion chamber wherein a vortex is established which rapidly removes the calcined clay from the combustion chamber. An apparatus suitable for this purpose is described in British Patent Specification No. 869,966. If necessary to ensure that the calcined clay contains at least 80% by weight of particles smaller than 2 microns e.s.d., the calcined clay can be comminuted by, for example, dry ball milling or fluid energy milling to break up any aggregates which form during the calcination step.

Uncalcined kaolin and kaolin calcined by the "soak calcination" method (in which the kaolin is exposed to a temperature greater than 500°C for a time greatly in excess of 5 seconds and usually more than 1 hour) both typically have a specific gravity in the range of from 2.5 to 2.7. In addition the specific surface area of soak calcined kaolin rarely exceeds 12 m²g⁻¹.

The elastomer of the elastomer compositions according to the second aspect of the present invention can be a natural rubber and/or a synthetic rubber. Examples of synthetic rubbers which can be employed are styrene-butadiene rubber (SBR), nitrile rubber, a polybutadiene, or a polyisoprene. The elastomer compositions will normally also contain conventional additives such as accelerators, vulcanising activators and processing aids. The filler in accordance with the first aspect of the invention can constitute the sole filler in the filled elastomer composition or it can be mixed in any proportions with other fillers, such as carbon black.

The invention is further illustrated by the following Examples.

40 EXAMPLE 1

A Dorset ball clay having a particle size distribution such that 4% by weight consisted of particles having an equivalent spherical diameter larger than 5 microns, 88% by weight consisted of particles having an equivalent spherical diameter smaller than 2 microns and 77% by weight consisted of particles having an equivalent spherical diameter smaller than 1 micron, was milled in order to break up aggregates and coarse particles. The milled ball clay had a particle size distribution such that there were no particles larger than 53 microns, 1.5% weight consisted of particles having an equivalent spherical diameter larger than 5 microns, 90% by weight consisted of particles having an equivalent spherical diameter smaller than 2 microns, and 80% by weight consisted of particles smaller than 1 micron. The milled clay was calcined by injecting it into a cyclone-shaped combustion chamber in which it was exposed to a temperature of 700°C for an average of about 1 second. The calcined clay had a particle size distribution such that 80% by weight of the particles had an equivalent spherical diameter smaller than 2 microns, a specific gravity of 2.2 and a specific surface area of 13 m²g⁻¹. Samples of the calcined clay were mixed with different amounts of 3-mercaptopropyltrimethoxysilane, and the coated clay samples were incorporated into a motor vehicle tyre carcass composition having the following ingredients:—

COMPOSITION

<i>Ingredient</i>	<i>Parts by weight</i>	
Natural rubber	50	
Styrene butadiene rubber	50	
5 Stearic acid	1.5	5
Zinc oxide	3.0	
Proprietary blend of non-staining antioxidants	2.0	
Pale coumarone resin	3.0	
N-cyclohexyl-2-benzothiazyl sulphenamide (CBS)	1.5	
10 Tetramethyl thiuram disulphide (TMTD)	0.1	10
Magnesium carbonate coated sulphur	2.0	
Fast extruding furnace carbon black (FEF)	54	
Silane treated calcined clay	26	

15 The stearic acid and zinc oxide are vulcanizing activators, the coumarone resin is a processing aid, the CBS is an accelerator, and the TMTD is a booster accelerator.

The ingredients were mixed and formed into a sheet on a roller mill at ambient temperature and the compound was vulcanised at 153°C for a time sufficient to give a 95% cure.

20 Samples of the vulcanised composition were then tested for modulus at 300% elongation, tensile strength, elongation at break, tear strength, compression set, tension set and abrasion loss. The results obtained are set forth in Table 1 below:—

TABLE 1

% by weight of silane based on weight of dry calcined clay		0	0.1	0.5	1.0	control	
Modulus at 300% elongation(MNm ⁻²)		9.2	10.0	11.9	11.3	12.0	
tensile strength (MNm ⁻²)		17.6	19.1	19.9	17.1	19.8	
30 elongation at break (%)		400	430	380	330	390	30
tear strength (kNm ⁻¹)		48.5	57.0	50.0	55.5	63.5	
compression set (%)		29.8	27.2	20.7	20.5	25.0	
tension set (%)		27.1	24.0	22.4	20.0	25.0	
abrasion loss (mm ³)		164	164	169	166	120	
35							35

40 The control composition was produced as described above except that the silane-treated calcined clay was replaced with an equal volume of a conventional reinforcing filler, viz semi-reinforcing furnace carbon black (SRF). It will be seen that the composition containing calcined clay treated with 0.5% by weight of the silane has substantially identical tensile strength properties to those of the control composition but superior compression set and tension set.

EXAMPLE 2

45 There were produced 2 further motor vehicle tyre carcass compositions having the same formulation as described in Example 1, except that the silane-treated calcined Dorset ball clay was replaced with a silane-treated calcined kaolin clay from S. Carolina, U.S.A. This latter kaolin clay had a particle size distribution such that substantially all of the particles had an equivalent spherical diameter smaller than 5 microns, 90% by weight consisted of particles having an equivalent spherical diameter smaller than 2 microns, and 70% by weight consisted of particles

50 having an equivalent spherical diameter smaller than 1 micron. The kaolin clay was calcined by injecting it into a cyclone-shaped combustion chamber in which it was exposed to a temperature of 700°C for an average time of about 1 second. The calcined clay had a particle size distribution such that 80% by weight consisted of particles having an equivalent spherical diameter smaller than 2 microns, a specific gravity of 2.2, and a specific surface area of 23

55 m²g⁻¹. The calcined clay was divided into two portions, one of which was mixed with 0.5% by weight, based on the weight of dry calcined clay of 3-mercaptopropyltrimethoxysilane and incorporated into a motor vehicle tyre carcass composition of the type described in Example 1, and the other portion was incorporated into such a motor vehicle tyre carcass composition without preliminary silane treatment.

60 Samples of the vulcanised compositions containing the silane-treated and the untreated calcined clay were tested for modulus at 300% elongation, tensile strength, elongation at break, tear strength, compression and tensile set, and the results obtained are set forth in Table II below.

TABLE II

	silane-treated calcined clay	untreated calcined clay	
5			5
modulus at 300% elongation (MNm ⁻²)	14.7	11.9	
tensile strength (MNm ⁻²)	20.1	19.9	
elongation at break (%)	350	385	
tear strength (kNm ⁻¹)	67.0	60.0	
10 compression set (%)	22.0	27.2	10
tension set (%)	20.5	22.4	

15 The compositions had roughly equivalent tensile properties, but the composition containing the silane-treated calcined clay had superior tear strength, compression set and tension set. 15

EXAMPLE 3

Further motor vehicle tyre carcass compositions were prepared according to the same formulation as set out in Example 1, except that no carbon black was used, the sole reinforcing filler being 104 grams of the calcined kaolin clay described in Example 2. One composition was prepared containing the calcined kaolin clay treated with 0.5% by weight, based on the weight of dry calcined kaolin, of 3-mercaptopropyltrimethoxysilane, and a second composition containing untreated calcined kaolin clay. Samples of the vulcanised compositions were tested for modulus at 300% elongation, tensile strength, elongation at break, tear strength, compression set and tensile set, and the results obtained are set forth in Table III below. 25

TABLE III

	silane-treated calcined clay	untreated calcined clay	
30			30
modulus at 300% elongation (mm ⁻²)	11.0	10.0	
tensile strength (MNm ⁻²)	19.1	19.0	
elongation at break (%)	525	572	
35 tear strength (Knm ⁻¹)	59.0	55.0	35
compression set (%)	28.5	30.0	
tension set (%)	29.0	30.0	

40 Again the compositions containing the silane treated calcined clay had superior tear strength, compression set and tension set properties. 40

EXAMPLE 4

45 Three further motor vehicle tyre carcass compositions were prepared according to the formulation described in Example 1, except that the silane-treated calcined Dorset ball clay filler was replaced by, respectively:— 45

(1) An uncalcined china clay from Cornwall having a specific gravity of 2.64, a specific surface area of 10.5 m²g⁻¹, and a particle size distribution such that 0.1% by weight consisted of particles having an equivalent spherical diameter larger than 10 microns and 80% by weight consisted of particles having an equivalent spherical diameter smaller than 2 microns. 50

(2) A calcined kaolin which was formed by exposing Clay (1) to a temperature of 1050°C for 1 hour. This calcined clay had a specific gravity of 2.6, and a specific surface area of 8.5 m²g⁻¹ and a particle size distribution such that 50% by weight thereof consisted of particles with an equivalent spherical diameter smaller than 2 microns. 55

(3) A calcined kaolin which was formed by injecting the S. Carolina kaolin clay which was used in Example 2 into a cyclone-shaped combustion chamber in which it was exposed to a temperature of 700°C for an average time of about 1 second. 60

In each case the clay or calcined clay filler was mixed with 0.5% by weight, based on the weight of dry clay, of 3-mercaptopropyltrimethoxysilane and incorporated into a motor vehicle tyre carcass composition of the type described in Example 1. Samples of the vulcanised compositions containing the silane-treated clays were tested for modulus at 300% elongation, tensile strength, tear strength, compression set, tension set and abrasion loss, and the results obtained are set forth in Table IV below:— 60

TABLE IV

Filler	(1)	(2)	(3)	
Modulus at 300% elongation(MNm ⁻²)	8.9	12.4	11.9	
5 tensile strength (MNm ⁻²)	18.9	18.9	19.5	5
tear strength (kNm ⁻¹)	58.5	60.0	68.5	
compression set (%)	28.2	24.0	22.6	
tension set (%)	27.0	20.0	12.0	
10 abrasion loss (mm ³)	168	171	151	10

It will be seen that only a small improvement in reinforcing properties, compared with those exhibited by the silane-treated uncalcined clay, is obtained with the silane-treated calcined clay which has been calcined at 1050°C for 1 hour. However a much greater improvement is achieved with the silane-treated calcined clay which has been calcined at 700°C for 1 second, especially in tear strength, compression and tension set and abrasion loss.

15 It is believed that the calcination conditions should be such that, after calcinations, the substantially dehydroxylated clay has a surface hydroxyl content of from 1 to 7, preferably 2 to 6, groups/mn² (compared with 10 to 12 hydroxyl groups/nm² for the uncalcined clay).

20 EXAMPLE 5

Four nitrile rubber hose compositions A, B, C and D were prepared according to the following formulations:

25	Parts by weight				25
	A	B	C	D	
Composition	100	100	100	100	
nitrile rubber	1	1	1	1	
stearic acid	5	5	5	5	
30 zinc oxide	2	2	2	2	30
antioxidant	15	15	15	15	
dioctylphthalate plasticiser	2	2	2	2	
sulphur	1.5	1.5	1.5	1.5	
dibenzthiazyl disulphide	0.4	0.4	0.4	0.4	
35 tetramethyl thiuram	130	130	130	0	35
monosulphide	0	0	0	90	
filler					
semi-reinforcing furnace					
carbon black					

40 In Composition A the filler was formed by injecting the S. Carolina kaolin clay which was used in Example 2 into a cyclone-shaped combustion chamber in which it was exposed to a temperature of 700°C for an average time of about 1 second. The calcined clay has a specific gravity of 2.2, a specific surface area of 23 m²g⁻¹ and a particle size distribution such that 80% by weight consisted of particles having an equivalent spherical diameter smaller than 2 microns.

45 No substituted silane was mixed with this filler.
In Composition B the filler was the same calcined kaolin clay as was used in Composition A but it was mixed with 0.65% by weight, based on the weight of dry calcined clay, of 3-mercaptopropyltrimethoxysilane.

50 In Composition C the filler was formed by exposing the kaolin clay described in Example 4 (1) to a temperature of 1050°C for 1 hour. This calcined clay has a specific gravity of 2.6, a specific surface area of 8.5 m²g⁻¹ and a particle size distribution such that 50% by weight consisted of particles having an equivalent spherical diameter smaller than 2 microns. The calcined clay was mixed with 0.65% by weight, based on the weight of dry calcined clay, of 3-mercaptopropyltrimethoxysilane.

55 Samples of the vulcanised compositions A, B, C and D were tested for modulus at 200% elongation, tensile strength, elongation at break and tear strength and the results obtained are set forth in Table V below.

TABLE V

Composition	A	B	C	D	
Modulus at 200% elongation (MNm ⁻²)	5.1	10.0	5.2	14.5	
5 Tensile strength (MNm ⁻²)	10.4	12.5	6.7	15.1	5
Elongation at break (%)	650	510	490	230	
Tear Strength (kNm ⁻¹)	100	135	63	110	

The results for Composition A show that when the filler is prepared by calcining a kaolin clay in accordance with the invention a composition is obtained which has a tear strength which is comparable with that of the conventional Composition D containing semi-reinforcing carbon black while at the same time having great flexibility as is shown by the high elongation at break.

Comparison of the results for Compositions B and C shows the greatly superior results which are obtained when the kaolin clay is calcined in accordance with the invention before being mixed with a substituted silane.

CLAIMS

1. A filler for use in elastomer compositions which filler comprises a substantially dehydroxylated clay which has a specific gravity not greater than 2.4 and a specific surface area (as measured by the B.E.T. liquid nitrogen adsorption method) of at least 10 m²g⁻¹.
2. A filler as claimed in claim 1 wherein the substantially dehydroxylated clay is a calcined kaolinitic clay.
3. A filler as claimed in claim 1 or 2, wherein said substantially dehydroxylated clay has a specific gravity not greater than 2.2.
4. A filler as claimed in claim 1, 2 or 3, wherein said substantially dehydroxylated clay has a specific surface area of at least 20 m²g⁻¹.
5. A filler as claimed in any one of claims 1 to 4 wherein the substantially dehydroxylated clay contains at least 80% by weight of particles smaller than 2 microns equivalent spherical diameter.
6. A filler as claimed in any one of claims 1 to 5, wherein said substantially dehydroxylated clay is treated with a substituted silane.
7. A filler as claimed in claim 6, wherein said substituted silane contains at least one aminoalkyl or mercaptoalkyl group and at least one hydroxy, hydroxyalkyl or alkoxy group.
8. A filler as claimed in claim 7 wherein said substituted silane can be represented by the general formula:



wherein R₁ is an aminoalkyl or mercaptoalkyl group, R₂ is a hydroxy, hydroxyalkyl or alkoxy group, and each of R₃ and R₄, which may be the same or different, is a hydrogen atom or hydroxy, alkyl, hydroxyalkyl or alkoxy group.

9. A filler as claimed in claim 8, wherein each of R₂, R₃ and R₄ is a hydroxy, hydroxyalkyl or alkoxy group.
10. A filler as claimed in claim 8 or 9, wherein each of R₁, R₂, R₃ and R₄ contains not more than 4 carbon atoms.
11. A filler as claimed in any one of claims 6 to 11, wherein the substantially dehydroxylated clay is coated with at least 0.05% by weight of the substituted silane.
12. A filler as claimed in claim 11, wherein the substantially dehydroxylated clay is coated with from 0.4% to 0.8% by weight, based on the weight of substantially dehydroxylated clay, of the substituted silane.
13. A filler as claimed in claim 1, substantially as described in any one of the foregoing Examples.
14. A filled elastomer composition which comprises an elastomer and a filler as claimed in any one of claim 1 to 13.
15. A filled elastomer composition as claimed in claim 14, wherein the elastomer is a natural rubber and/or a synthetic rubber.

16. A filled elastomer composition as claimed in claim 14, substantially as described in any one of the foregoing Examples.

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